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Consider a channel or passage connecting compartments A and B that is wide enough so that two particles in the channel can pass one another. It is the purpose of this paper to derive the laws giverning the flow of particles in either direction through such a channel.

$$\text{Side A}\ \underset{a}{\nearrow}\ \overline{\underline{a\ {}^{a}\ b\ {}^{a}\ a\ b\ {}^{b}\ b}}\ \underset{b}{\nwarrow}\ \text{Side B}$$

The position of a particle in the channel can be found by projecting the centers of all the particles onto the axis of the channel. If a particular point is k from the left, then the particle to whose center the point corresponds is in the k^{th} position. The assumption is that the centers of any two particles will project onto different points of the axis.

An event occurs if a particle enters the channel from either side A or B . It may either strike a given particle in the channel with probability r , or bypass it with probability $s = 1 - r$. If it bypasses the particle, it will contirue moving, and either strike or bypass the next particle along its path. If, on the other hand, it strikes (say) particle k , the moving particle comes to rest in position k , and the struck particle moves in the direction of the original motion. Thus, if a particle enters from A , any particle it strikes will move toward B . Also, once a particle is moving, it follows the same laws of motion as the entering particle.

We have assumed here that the probability r , that a moving particle strikes a stationary particle in position k , is independent of k . With or without this assumption, however, when an event occurs, exactly one particle will move to position k and one particle will continue beyond position k for every k. Hence, the motion traverses every position in the channel, and any particle may be struck.

If we adopt these laws of motion, we may conclude that if a particle enters from A, sooner or later a particle, though not necessarily the same one, will exit into side B. Hence, the channel always holds the same number of particles n. We let n be the length of the channel.

We will assume that simultaneous entries from both sides do not occur. Similarly, we shall say that once a particle enters the channel, it is such a short time before some particle leaves the channel as a result, that no other entry occurs before this happens. This assumption is stronger than necessary, but it has the advantage of simplicity.

Finally, we let 'p' be the probability that the next entry will be from side A, and $q = 1 - p$ be the probability that the next entry will be from side B. Then we can calculate the probability that a particle in position k will move toward (say) side B, as a result of an entry. Clearly this requires an entry from side A, and that some combination of particles hitting and bypassing others results in the particle which is moving striking particle k, when the motion reaches position k. For $k = 1$, clearly,

$$\text{pr(particle 1 moves toward B)} = pr$$

For $k = 2$, the entering particle may miss particle 1 and hit 2, with <u>prob =</u> <u>prs</u>, or hit 1, which then strikes 2, with <u>prob = pr^2</u>. Thus,

$$\begin{aligned}\text{pr(particle 2 moves toward B)} &= prs + pr^2 \\ &= pr(s + r) \\ &= pr\end{aligned}$$

Similarly, for $k = 3$, the entering particle can miss 1 and 2, and hit

3, with prob $= prs^2$, or miss 1 and hit 2, which then strikes 3, with prob $= pr^2s$, or it can hit 1, which then may miss 2 and hit 3, with prob $= pr^2s$, or the entering particle may hit 1, which may hit 2, which in turn strikes 3, with prob $= pr^3$. Then:

$$
\begin{aligned}
pr(\text{particle 3 moves toward B}) &= prs^2 + 2pr^2s + pr^3 \\
&= pr(s^2 + 2rs + r^2) \\
&= pr(s+r)^2 \\
&= pr
\end{aligned}
$$

In general, there are $\binom{k-1}{j}$ ways in which j of the first $k-1$ particles may move while the others stand still. Hence, the probability that this occurs is just:

$$pr(\text{exactly } j \text{ of the first } k\text{-1 are struck}) = \binom{k-1}{j} r^j s^{k-j-1}$$

and the probability that the k^{th} will be struck is just:

$$
\begin{aligned}
pr(k \text{ will move toward B}) &= pr \sum_{j=0}^{k-1} \binom{k-1}{j} r^j s^{k-j-1} \\
&= pr(r+s)^{k-1} \\
&= pr
\end{aligned}
$$

One can argue this another way. Since r is the probability that the moving particle will hit a given particle, r should be the probability that the given particle will be hit by the moving particle. Thus pr is the probability that it is hit from A , and hence moves toward B . Similarly, the probability that particle k will move toward A is qr . Then the probability that k will move is $pr + qr = r$, and the probability that it remains stationary is a result of an entry is $1-r = s$.

Now it is easy to calculate the probability that particle k , once it is moving toward B , will jump to position j , for $j > k$. It must miss all the $(j-k-1)$ particles between, with probability s^{j-k-1} , and strike j . Thus,

$$pr(k \to j \mid k \text{ moves toward B}) = \begin{cases} s^{j-k-1}r & \text{if } j > k \\ s & \text{if } j = k \\ 0 & \text{otherwise} \end{cases}$$

and

$$pr(k \to j \mid k \text{ moves toward A}) = \begin{cases} s^{k-j-1}r & \text{if } j < k \\ s & \text{if } j = k \\ 0 & \text{otherwise} \end{cases}$$

Hence, we can easily calculate the unconditional probability that k will move to j as a result of the next entry.

$$pr(k \to j) = pr(k \to j \mid k \text{ moves toward B}) \cdot pr(k \text{ moves toward B})$$

$$+ \; p(k \to j \mid k \text{ moves toward A}) \cdot pr(k \text{ moves toward A})$$

Or

$$p(k \to j) = \begin{cases} pr^2 s^{j-k-1} & \text{if } j > k \\ qr^2 s^{k-j-1} & \text{if } j < k \\ s & \text{if } j = k \end{cases}$$

We list below all the possible movements k can undergo as a result of an entry and their probabilities, as well as the probability of movements which originate or end at either side A or B .

1) For a particle in the channel at position k to move to position j , as a result of the next entry:

$$p(k \rightarrow j) = \begin{cases} pr^2 s^{j-k-1} & , \text{ if } j > k \\ qr^2 s^{k-j-1} & , \text{ if } j < k \\ s & , \text{ if } j = k \end{cases}$$

2) For a particle in the channel at position k to move to either side:

$$p(k \rightarrow \text{side B}) = prs^{n-k}$$

$$p(k \rightarrow \text{side A}) = qrs^{k-1}$$

3) For a particle entering the channel to come to rest at position k :

$$p(\text{side A} \rightarrow k) = prs^{k-1}$$

$$p(\text{side B} \rightarrow k) = qrs^{n-k}$$

4) For a particle to move from one side to the other, never striking a particle in the channel:

$$p(\text{side A} \rightarrow \text{side B}) = ps^{n}$$

$$p(\text{side B} \rightarrow \text{side A}) = qs^{n}$$

What we wish to find is the probability f_A that a particle will move from side A to B given an entry, and the probability f_B of a movement from B to A .

$$(1)\qquad \begin{cases} f_A = p\left(\sum\limits_{k=1}^{n} rs^{n-k}y_k + s^n\right) \\[2em] f_B = q\left(\sum\limits_{k=1}^{n} rs^{k-1}\overline{y}_k + s^n\right) \end{cases}$$

where y_k = the probability of finding an 'a' particle in position k ,

$\overline{y}_k = 1-y_k$ = the probability of finding a 'b' particle in position k .

Thus, we must first find an expression for the y's and $\overline{y}$'s . However, if the channel is in steady state, this is not hard to do.

$$(2)\qquad y_k = sy_k + prs^{k-1} + \sum_{j=1}^{k-1} pr^2s^{k-j-1}y_j + \sum_{j=k+1}^{n} qr^2s^{j-k-1}y_j$$

Fortunately, it is unnecessary to solve for all of the y_k's explicitly.

$$f_A = \sum_{k=1}^{n} prs^{n-k}y_k + ps^n$$

$$= \sum_{k=1}^{n-1} prs^{n-k}y_k + pry_n + ps^n$$

But $y_n = sy_n + prs^{n-1} + \sum\limits_{k=1}^{n-1} pr^2s^{n-k-1}y_k$.

If $r \neq 0$,

$$y_n = ps^{n-1} + \sum_{k=1}^{n-1} prs^{n-k-1} y_k$$

Or $$sy_n = ps^n + \sum_{k=1}^{n-1} prs^{n-k} y_k$$

So: $f_A = (pr + s)y_n = \underline{(1-qr)y_n}$

(3)

Similarly, $f_B = (qr + s)\overline{y}_1 = \underline{(1-pr)\overline{y}_1}$

As for the special case $r = 0$.

Then $f_A = p$, $f_B = q$ (from (1)), and the equations (2) reduce to:

$$y_k = y_k$$

<u>Lemma 1.</u> $y_n = \frac{p(1-qr)^{n-1}}{D_n}$, for $0 < r \leq 1$, where D_n = the determinant

of

$$\begin{vmatrix} 1 & -qr & -qrs & \cdots & -qrs^{n-2} \\ -pr & 1 & -qr & \cdots & -qrs^{n-3} \\ -prs & -pr & 1 & & -qrs^{n-4} \\ \vdots & & & & \vdots \\ -prs^{n-2} & -prs^{n-3} & -prs^{n-4} & & 1 \end{vmatrix}$$

Note that this matrix, post-multiplied by the vector $(y_1 , y_2 ,\ldots,y_n)^T$, should yield $p(1,s,s^2,\ldots,s^{n-1})^T$, if equations (2) are to be satisfied for $r \neq 0$.

Proof: Following Cramer's rule,

$$D_n y_n = \left| \begin{array}{cccc} 1 & -qr & -qrs \;\ldots & p \\ -pr & 1 & -qr \;\ldots & ps \\ -prs & -pr & 1 & ps^2 \\ \vdots & \vdots & \ddots & \vdots \\ -prs^{n-2} & -prs^{n-3} & \cdots & ps^{n-1} \end{array} \right|$$

We can move the last column (which is just the right-hand side of the problem noted) to the first position. Since it will pass $(n-1)$ columns, this will change the sign by $(-1)^{n-1}$.

$$(-1)^{n-1} D_n y_n = \left| \begin{array}{cccc} p & 1 & -qr & qrs^{n-3} \\ ps & -pr & 1 & \\ ps^2 & -prs & -pr & \\ \vdots & \vdots & \vdots & -pr \\ & & & 1 \\ ps^{n-1} & -prs^{n-2} & & -pr \end{array} \right|$$

By successively adding $(-s)$ times a row to the row below it (starting with row $n-1$) , we achieve an upper-triangular structure.

$$(-1)^{n-1} D_n y_n = \left| \begin{array}{cccc} p & & & \\ & (-s-pr) & & \text{Garbage} \\ & & (-s-pr) & \\ & 0 & & \\ & & & (-s-pr) \end{array} \right|$$

What the garbage is does not matter, for the determinant of the matrix is just the product of its diagonal terms.

$$(-1)^{n-1}D_n y_n = p(-s-pr)^{n-1} = p(1-qr)^{n-1}(-1)^{n-1}$$

Hence,

$$(4) \qquad y_n = \frac{p(1-qr)^{n-1}}{D_n}$$

(The restriction on r is necessary to put equations (2) into the appropriate form.)

Corollary

$$(5) \qquad \bar{y}_1 = \frac{q(1-pr)^{n-1}}{D_n}$$

This follows from the symmetry of the problem.

Lemma 2. Consider D_n as a function of p. Then

$$D_n(p) = \frac{p(1-qr)^n - q(1-pr)^n}{p-q} \quad \text{for } p \neq 1/2$$

$$D_n(1/2) = \lim_{p \to 1/2} D_n(p)$$

Proof: $D_n(p)$ is a determinant. Hence, it is defined as a polynomial in p, in this case, considering r fixed. Thus, as defined, $D_n(p)$ is continuous in p.

If $D_n(p)$ as derived $= D_n(p)$ as defined, for all $p \neq 1/2$, then $\lim_{p \to 1/2} D_n(p)$ as derived is the same as $\lim_{p \to 1/2} D_n(p)$ as defined $= D_n(1/2)$ as defined.

Hence, if we can show that:

$$D_n(p) = \frac{p(1-qr)^n - q(1-pr)^n}{p-q} \tag{6}$$

we are justified in letting

$$D_n(1/2) = \lim_{p \to 1/2} D_n(p) \qquad .$$

To show (6), look at D_{n+1} .

$$D_{n+1} = \begin{vmatrix} 1 & -qr & qrs & & -qrs^{n-1} \\ -pr & 1 & qr & & \\ -prs & -pr & 1 & & \\ & & & \ddots & -qr \\ -prs^{n-1} & & & -pr & 1 \end{vmatrix}$$

Adding $(-s)x$ the second row to the first and expanding on the new first row, we get:

$$D_{n+1} = (1 + prs)\, D_n + (s + qr)\,(-r)\,(-1)^n\, D_n y_1^{(n)}$$

where $y_1^{(n)}$ = the probability of finding an 'a' in position one of a tunnel of length n .

Letting $y_1^{(n)} = 1 - \bar{y}_1^{(n)}$, and substituting from the corollary of Lemma 1,

$$D_{n+1} = (1-qr)\, D_n + qr(1-pr)^n \qquad .$$

We could have added $(-s)x$ the second column to the first and expanded on the new first column just as easily. This would yield:

$$D_{n+1} = (1-pr)\,D_n + pr(1-qr)^n$$

For $p \neq 1/2$, these two expressions can be solved for D_n.

$$D_n = \frac{pr(1-qr)^n - pr(1-pr)^n}{(1-qr) - (1-pr)}$$

or

$$D_n = \frac{p(1-qr)^n - q(1-pr)^n}{p-q}$$

(This proof is due to Dr. S. Levin. An alternate inductive proof is also possible.) Q.E.D.

Now e can prove:

<u>Theorem 1</u> $(f_A - f_B) = p-q$, independent of n and r.

<u>Proof:</u> Trivial for $r = 0$, since $f_A = p$, and $f_B = q$.

(3) For $r \neq 0$, $f_A = (1-qr)y_n$

$$f_B = (1-pr)\bar{y}_1$$

So:

$$f_A - f_B = (1-qr)\ \frac{p(1-qr)^{n-1}}{D_n} - \frac{(1-pr)q(1-pr)^{n-1}}{D_n}$$

$$= \frac{p(1-qr)^n - q(1-pr)^n}{\left(\frac{p(1-qr)^n - q(1-pr)^n}{p-q}\right)}$$

(7) $\underline{f_A - f_B = p-q}$ Q.E.D.

Perhaps more interesting is

<u>Theorem 2:</u> $\dfrac{f_A}{f_B} = \dfrac{p(1-qr)^n}{q(1-pr)^n}$, for $0 \leq r \leq 1$.

Proof: At $r = 0$, $\dfrac{f_A}{f_B} = \dfrac{p}{q}$, from the special case mentioned earlier. At any other r ,

$$\frac{f_A}{f_B} = \frac{(1-qr)y_n}{(1-pr)y_1} = \frac{p(1-qr)^n/D_n}{q(1-pr)^n/D_n}$$

(8) $$\frac{f_A}{f_B} = \frac{p(1-qr)^n}{q(1-pr)^n}$$ Q.E.D.

f_A and f_B are merely probabilities that flow will occur in one direction or the other as a result of a single entry. To calculate the actual rate of flow we must replace the probability of an entry from either side with the rate at which entries from either side occur. For a chemical solution, we allow these rates on either side to be proportional to the concentration of the entering particles on that side, but not necessarily with the same proportionality factor. Differences could occur because of a temperature difference, a pressure difference, or an electric potential difference between the ends of the channel.

Also, since many different types of particles might enter from either side, we must let the entry rate from each side to be a weighted sum of the concentrations of the entering particles. The weights will be called entry constants, and designated by μ_i (for side A) and μ_i' (for side B) . Similarly, C_i = concentration of the i^{th} entering species on side A ,

C_i' = concentration on side B .

Then
$$p = k \sum \mu_i C_i$$

$$q = k \sum \mu_i' C_i' \quad .$$

Now define

$$\lambda = \frac{p}{q} = \frac{\Sigma\, \mu_i C_i}{\Sigma\, \mu_i' C_i'}$$

$$\beta = \frac{1-qr}{1-pr} = \frac{\lambda + s}{1 + \lambda s}$$

Then:

(9)
$$F_A = (\Sigma\, \mu_i C_i)\beta^n \; \frac{1-\lambda}{1-\beta^n \lambda}$$

$$F_B = (\Sigma\, \mu_i' C_i') \; \frac{1-\lambda}{1-\beta^n \lambda}$$

Let us examine the theory.

I. Limiting Cases

As $s \to 0$ we should have a tunnel. But, $\lim_{s \to 0} \beta = \lambda$. Hence,

$$F_A = \Sigma\, \mu_i C_i \; \lambda^n \left(\frac{1-\lambda}{1-\lambda^{n+1}}\right)$$

$$F_B = \Sigma\, \mu_i' C_i' \quad \left(\frac{1-\lambda}{1-\lambda^{n+1}}\right)$$

So:

$$(10) \qquad F_A = \lambda^n \frac{\Sigma \mu_i C_i}{\Sigma \mu_i' C_i'} = \lambda^{n+1}$$

$$\text{and} \quad F_A - F_B = (\Sigma \mu_i C_i - \Sigma \mu_i' C_i') \quad .$$

These two equations characterize a tunnel. Hence, this limiting case is valid.

<u>As $s \to 1$</u> we should approximate simple diffusion. Note that

$$\lim_{s \to 1} \beta = 1 \ .$$

Thus,

$$F_A = \Sigma \mu_i C_i$$

$$F_B = \Sigma \mu_i' C_i'$$

Hence,

$$(11) \qquad \frac{F_A}{F_B} = \lambda$$

$$F_A - F_B = \Sigma \mu_i C_i - \Sigma \mu_i' C_i'$$

Again, these equations characterize simple diffusion.

II. Approximation

We can try to approximate a semi-narrow channel by a composite channel; that is, a weighted average of a free diffusion path and a narrow tunnel. We can assign weighted η to the tunnel and $(1-\eta)$ to the diffusion path. If F^T, F^P, and F^S denote flow through the tunnel, diffusion path, and semi-narrow channel, we wish:

$$\eta\, F_A^T + (1-\eta)\, F_A^D = F_A^S$$

$$\bar{\eta}\, F_B^T + (1-\bar{\eta})\, F_B^D = F_B^S$$

Substituting:

$$\eta\left(\mu^T C_a\, \lambda^m \left(\frac{1-\lambda}{1-\lambda^{m+1}}\right)\right) - (1-\eta)\mu^D C_a = \mu^S C_a \beta^n \left(\frac{1-\lambda}{1-\beta^n\lambda}\right)$$

or

$$\eta = \frac{\left[\mu^S\left(\frac{1-\lambda}{1-\beta^n\lambda}\right)\beta^n - \mu^D\right]}{\left[\mu^T\left(\frac{1-\lambda}{1-\lambda^{m+1}}\right)\lambda^m - \mu^D\right]}$$

where the n = the length of the semi-narrow channel, which is known, and m = the length of the tunnel, which is to be determined.

$$\bar{\eta} = \frac{\mu^S\left(\frac{1-\lambda}{1-\beta^n\lambda}\right) - \mu^D}{\mu^T\left(\frac{1-\lambda}{1-\lambda^{m+1}}\right) - \mu^D}$$

For an exact solution, we must have $\bar{\eta} = \eta$. This condition is satisfied if we let:

$$\mu^D = \mu^S$$

and

$$\mu^T = \mu^S \quad .$$

Then η and $\bar{\eta}$ reduce to:

$$\eta = \bar{\eta} = \frac{(1-\beta^n)(1-\lambda^{m+1})}{(1-\beta^n\lambda)(1-\lambda^m)}$$

Think of η as a function of λ , and let $\lambda \to 0$. Then

$$\eta(0) = 1 - s^n \text{ , since } \beta = \frac{\lambda + s}{1 + \lambda s} \quad .$$

If η is to be constant, then:

$$(1-\beta^n)(1-\lambda^{m+1}) = (1-s^n)(1-\beta^n\lambda)(1-\lambda^m) \quad .$$

Or, substituting for β ,

$$[(1+\lambda s)^n - (\lambda+s)^n]\ [1-\lambda^{m+1}] = (1-s^n)[(1+\lambda s)^n - \lambda(\lambda\ s)^n](1-\lambda^m) \quad .$$

Comparing constant and first order coefficients of both polynomials, we get that these relations must hold:

$$(1-s^n) = (1-s^n) \qquad \text{(constant terms)} \quad .$$

and

$$(n\lambda s - ns^{n-1}\lambda) = (1-s^n)[n\lambda s - \lambda s^n] \qquad \text{(first-order terms)} \text{ .}$$

Or

$$s^{n-2} = s^{n-1} + s^n - s^{2n-1} \quad .$$

This is clearly untrue. Thus, a semi-narrow channel is not a composite.

However, if we examine η more, we see that

$$\eta = \frac{1 - \beta^n - \lambda^{m+1} + \beta^n\lambda^{m+1}}{1 - \beta^n\lambda - \lambda^m + \beta^n\lambda^{m+1}} \quad .$$

Restricting $\eta \leq 1$,

$$1 - \beta^n - \lambda^{m+1} + \beta^n\lambda^{m+1} \leq 1 - \beta^n\lambda - \lambda^m + \beta^n\lambda^{m\ 1} \quad .$$

Or

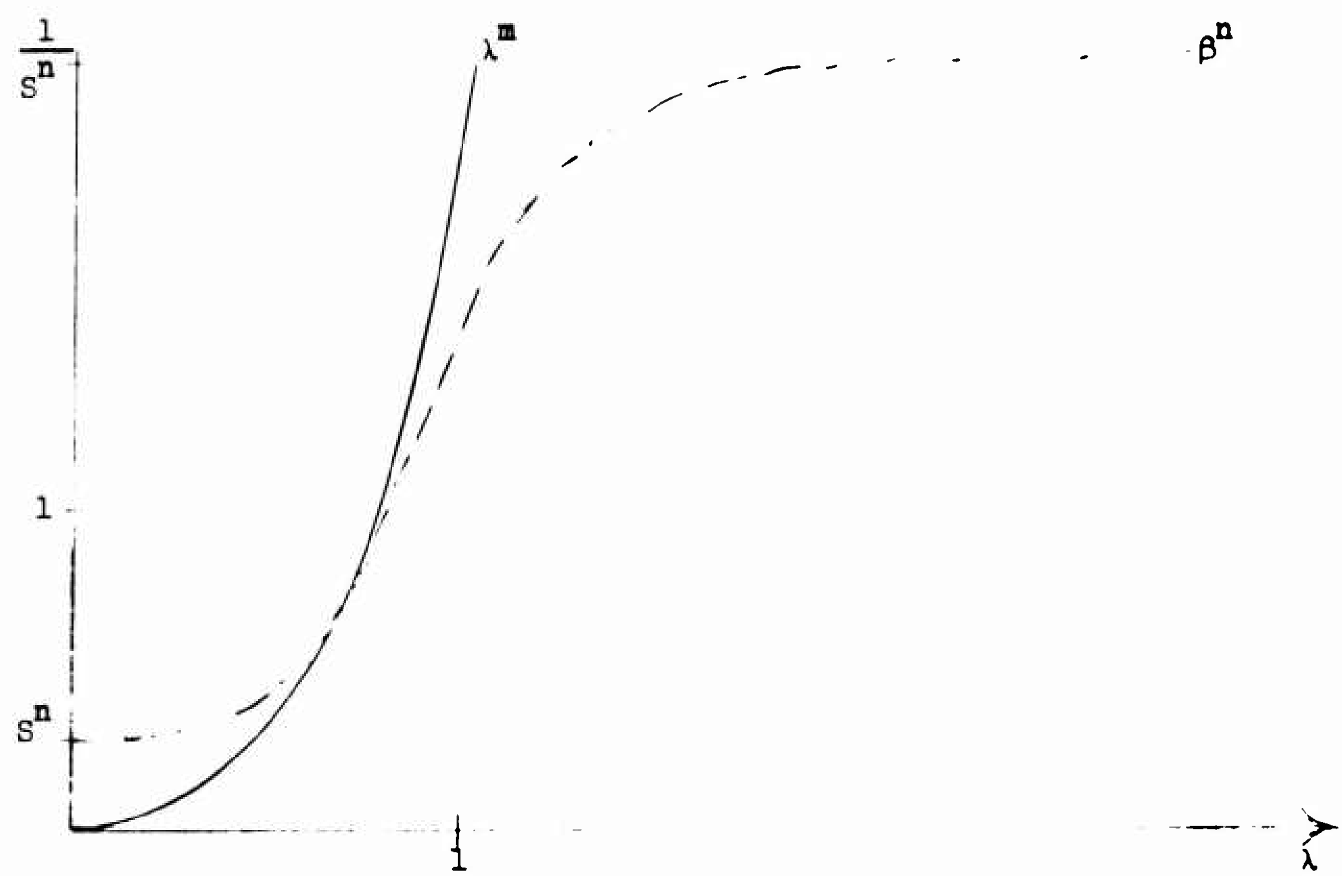
$$\beta^n(\lambda - 1) \leq \lambda^m(\lambda - 1)$$

Thus,

$$\beta^n \leq \lambda^m \qquad \text{for} \quad \lambda > 1$$

$$\beta^n \geq \lambda^m \qquad \text{for} \quad \lambda < 1 \qquad .$$

If we graph the two functions of λ , that is, β^n and λ^m , we see the following:



If, for some region around $\lambda = 1$, we can choose m so that:

$$\beta^n \approx \lambda^m ,$$

then we have $\eta = 1$, and that for λ near 1 , the semi-narrow channel of length n acts like a tunnel of length m . We find the value m by equating the derivatives at $\lambda = 1$. This is a first-order approximation.

$$n\beta^{n-1}\frac{d\beta}{d\lambda} = m\lambda^{m-1}$$

Now

$$\beta = \frac{\lambda+S}{1+\lambda S}$$

$$\frac{d\beta}{d\lambda} = \frac{1-S^2}{(1+\lambda S)^2}$$

Evaluating at $\lambda = 1$,

$$m = n\left(\frac{1-S}{1+S}\right)$$

Notice that as n gets very large, the approximation is valid over a larger and larger range. In fact, for $n \to \infty$, the semi-narrow channel becomes a tunnel, just as for $n \to 0$, the semi-narrow channel is the same as a diffusion path.

III. Flows Against the Gradient

Notice that the flow ϕ_i of the i^{th} entering species is just:

$$\phi_i = \left\{\mu_i\, C_i\, \beta^n - \mu_i'\, C_i'\right\}\left[\frac{1-\lambda}{1-\beta^n\lambda}\right]$$

Even if $\mu_i C_i < \mu_i' C_i'$ provided $\beta > 1$, and n is large enough, i.e., if $\beta^n > \frac{\mu_i C_i}{\mu_i C_i}$, or if $\frac{C_i'}{C_i} < \frac{\mu_i}{\mu_i'}\beta^n$ we can have species i flow against its gradient. Note here that when $\lambda > 1$, then $\beta > 1$, and $\beta < \lambda$, so that a tunnel of length n will transport species i against a higher gradient than a semi-narrow channel.

IV. Diffusion vs. Osmotic Diffusion Coefficients

In the human red blood cell, measurements of permeability to water are made in two ways. If an actual osmotic pressure is introduced, the net rate of flow of H_2O can be measured and an osmotic coefficient calculated. If osmotic balance is achieved, a diffusion coefficient can be calculated from the unidirectional water flow as measured with labeled water, or DHO. The surprising fact is that:

$$\mu_{osm} = 2.5\ \mu_{diff}.$$

Such a difference is readily explained by this theory. Let us propose channels of a semi-narrow type through which only water flows, to a first and probably good approximation. Then we assume equal temperature and pressure on both sides of these channels, and we say that water is unaffected by the membrane potential. Thus, the entry constants are the same from each side. Finally, we treat DHO as if the channel cannot distinguish it from H_2O.

If there is an osmotic gradient:

$$F_A - F_B = \mu(C-C') \quad .$$

Thus,

$$\underline{\mu_{osm} = \mu}$$

Now, if osmotic equilibrium is the case, then $\lambda = \beta = 1$. But:

$$\lim_{\lambda \to 1} \left(\frac{1-\lambda}{1-\beta^n \lambda} \right) = \lim_{\lambda \to 1} \frac{(1-\lambda)}{1-\lambda\left(\frac{\lambda+s}{1+\lambda s}\right)^n}$$

Using L'hopital's Rule: $= \dfrac{1}{n\dfrac{(1-s)}{(1+s)} + 1}$

and $\mu_{diff} = \dfrac{\mu}{n\dfrac{(1-s)}{(1+s)} + 1}$

Clearly, for $s < 1$, $\mu_{diff} < \mu_{osm}$. If we put in numbers:

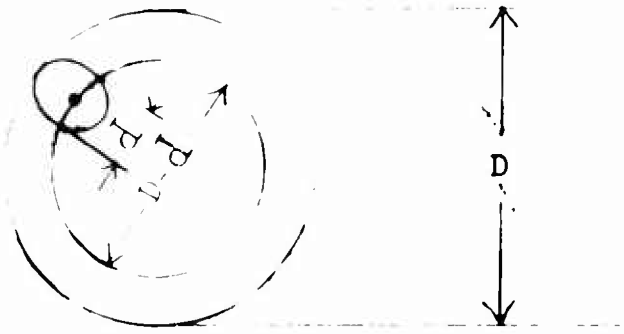
$$\frac{\mu_{osm}}{\mu_{diff}} = n\frac{(1-s)}{(1+s)} + 1 = 2.5$$

To calculate r, let:

> d = the diameter of an entering particle, where we assume all particles are of equal size.
>
> D = diameter of the channel, letting both be circular.

Then to enter the channel, the center of the particle must be somewhere in an area

$$S = \frac{\pi(D-d)^2}{4}$$



If the particle is to strike another, the centers of the two particles must be within d of one another, giving a "striking area" of

$$S = \frac{\pi d^2}{4}$$

We let $r = \frac{S}{A} = \frac{d^2}{(D-d)^2}$, when this is less than one. Hence,

$$r = \begin{cases} \dfrac{d^2}{(D-d)^2}, & \text{for } d < \frac{D}{2} \\ 1, & \text{for } D \geq \frac{D}{2} \end{cases}$$

Now, the size of a water molecule is said to be about $3\mathring{A}$, and the length of the channel, which we assume is just the thickness of the membrane, is 100A . Assuming close packing of particles in the channel (i.e., each molecule requires only $3\mathring{A}$ of length).

$$n = \frac{100}{3} = 33$$

Thus, if

$$n\left(\frac{1-s}{1+s}\right) = 1.5$$

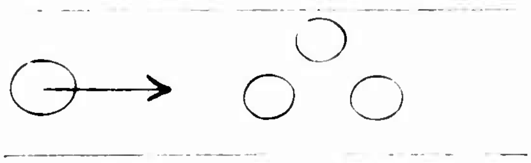
$$s = .914$$

$$\text{or } r = .086 \quad .$$

This gives $D = 13.2\mathring{A}$.

This model thus predicts that water channels will have a diameter of $13.2\mathring{A}$. Solomon has indirectly measured the channels and calculates that their diameter is about $10\mathring{A}$. We are, then, at least in the right ball park. If we do not assume close packing, and instead let fewer water molecules reside in the channel, then the channel diameter is smaller. Thus, $13.2\mathring{A}$ is an upper bound. Similarly, $\frac{\mu_{osm}}{\mu_{diff}}$ may be greater than 2.5 . This is the smallest measurement in the literature. As the ratio grows, the channel will shrink.

Although the mathematics are ironclad, this model of flow through semi-narrow channels is only an approximation to what may really happen. Some of its weaknesses are obvious. For example, we assumed that the probability r of a hit was independent of the position in the channel which the struck particle occupied. One might relax this assumption and subscribe to the belief that particles near the end of the channel should be easier (or harder) to hit than those in the center. One reason that particles near the end of the channel might escape being struck as often as those in the center could be that center particles could be packed more densely than the end particles, and hence fill up a greater part of the cross-sectional area of the center of the channel. In the figure, one can see how this might operate.



The moving particle would be certain to strike one of the particles.

A second weakness of the model is that it assumes that any particle which enters the channel has the same chance of hitting a given particle k as any other entering particle, whereas one entering particle may be of a different size than another. If, for example, we suppose that two particles of different sizes are permitted in the channel with diameters $d_1 < d_2$, a particle of type 1 would be less likely to strike another of type 1 than of type 2. Similarly, a particle of type 2 would be less likely to strike one of the first type than the second. In fact, a channel could act like a tunnel to the larger particle, and a semi-narrow channel to the smaller. If, for example, $d_2 = \frac{D}{2} + \epsilon$, and $d_1 \ll \frac{D}{2}$, then we might have a channel operating as a tunnel for large particles (type 2) and as a free diffusion channel for the small (type 1) particles. Alternately, a large particle might act as an effective plug to smaller ones, and hence slow down or stop what would otherwise be nearly free diffusion. In short, this model can and should be refined.

REFERENCES

1. Dantzig, G. B., Molecular-Sized Channels and Flows Against the Gradient, Operations Research Center, University of California, Berkeley, No. 31, October 1962.